QUANTITATIVE ZINC SPECIATION IN SOILS

Attacking Complexity with Complementary X-Ray Techniques

A scientific approach to cleaning up the environment requires basic chemical information at the molecular level about contaminants. For example, a remediation strategy depends not just on the concentration of the toxic metal but on its mobility in soil and water and its ease of uptake by plants, animals, and people, properties that depend on the chemical compounds containing the metal. A team of French researchers working at the Advanced Light Source (ALS) and the European Synchrotron Radiation Facility (ESRF) in Grenoble has shown how to use complementary x-ray techniques to identify zinc-containing compounds in contaminated French and Belgian soils located near smelters. In particular, they combined spatially resolved (at the μm scale) x-ray fluorescence (μ-XRF) and extended x-ray absorption fine structure (μ-EXAFS) at the ALS and polarized EXAFS at the ESRF to make the key identification of important zinc constituents and their structural forms (i.e., their speciation).

Like other toxic metals, such as chromium and uranium, zinc undergoes many chemical transformations during its journey from the source to the final resting place. The pyrometallurgical Imperial Smelting Process used for many decades in Europe produced considerable amounts of dust and fumes rich in zinc and lead. When the zinc reached the soil, it was deposited in the form of a number of "primary" zinc-containing minerals. Weathering of these minerals resulted in the trapping of zinc in "secondary" minerals, predominantly clay minerals but to a lesser extent iron oxyhydroxides and manganese oxides that immobilize the zinc, rendering it less harmful.

In recent years, x-ray diffraction and EXAFS of powder samples have been replacing older chemical-extraction techniques for speciation of contaminants in the environment. Making EXAFS measurements for a large number of compounds in well-prepared forms results in a library of standards that can be used when a sample contains multiple chemical compounds containing the same element. Mathematically fitting a combination of the EXAFS spectra from standards with the measured spectrum in principle identifies and gives the concentration of each compound in the sample. However, the method does not work well when too many standards are required, so it is necessary to have some idea of what is present, a difficult task when some compounds exist in small concentrations against a larger background of other compounds.

The French team attacked this problem for its soil samples by exploiting the newer third-generation synchrotron-radiation sources. Powder EXAFS hinted that zinc-containing clay minerals were the predominant species. Because of the layered structure of clays, EXAFS spectra with linearly polarized light has a distinctive angular dependence as an oriented sample is rotated in the beam, and this is what the team observed at the ESRF. A detailed analysis of the spectra revealed the local structure around the zinc in the clay.

The two next most important zinc species (i.e., the iron oxyhydroxides and manganese oxides) were identified at the ALS. First, with μ-XRF the team located regions containing manganese, iron, and zinc in these inhomogeneous samples. In particular, they found iron-rich grains that typically were 10 to 20 μm in size and manganese-rich spherules much larger at 300 μm. Application of μ-EXAFS within these regions then revealed the identity and structure of the zinc species. For example, the zinc-containing manganese compound was birnessite, a layered compound in which the zinc was adsorbed in the interlayer space above and below vacant sites with either four- or six-fold coordination. Model compounds derived from polarized and μ-EXAFS data were then used to obtain good fits of powder-EXAFS data for all the soil samples studied. ∎

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A. Manceau, B. Lanson, M. L. Schlegel, J.-C. Hargé, M. Musso, L. Eybert-Bérard, J.-L. Hazemann, D. Chateigner, and G. M. Lamble, "Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy," *Am. J. Sci.* (in press, 2000).

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## *Attacking Complexity with Complementary X-Ray Techniques*

- **Scientific approach to cleaning up the environment**
  - *Speciation at molecular level guides choice of remediation strategies*
  - *Electronic structure (oxidation state, chemical bonding)*
  - *Binding form (discrete compound, organic complex, adsorbate, ...)*

- **Extended X-ray Absorption Fine Structure (EXAFS)**
  - *Identifies species, their local structures, and their proportions*
  - *Based on comparisons with standard reference compounds*
  - *Requires additional information to solve complex samples*

- **Where is zinc in contaminated soils?**
  - *Polarized EXAFS at the ESRF identifies layered clay minerals*
  - *Micro EXAFS at the ALS reveals discrete manganese and iron minerals*
  - *Models and constraints for quantitative fits of powder EXAFS spectra*

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## Attacking Complexity with Complementary X-Ray Techniques

Micro x-ray fluorescence maps of elemental distributions show that zinc (center) is partitioned between large maganese-rich spherules (left) and smaller iron-rich grains (right) in a soil sample.
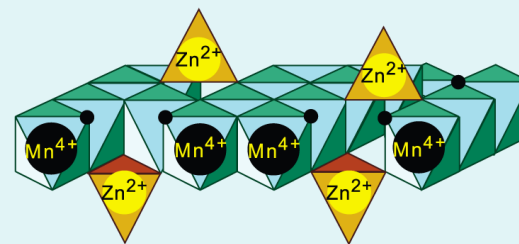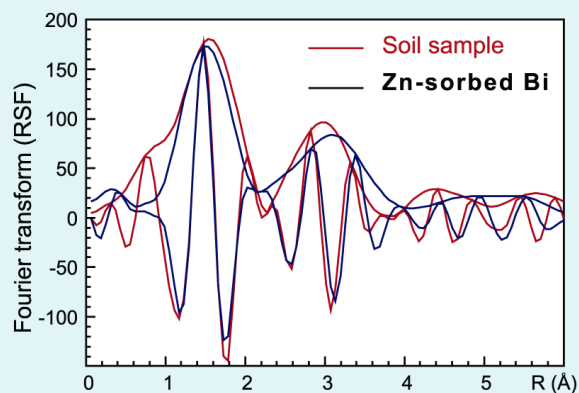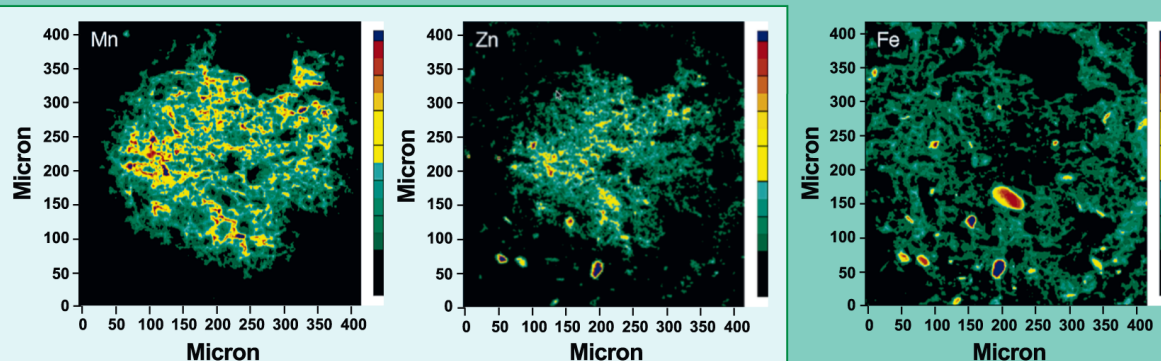
Micro EXAFS (red) of zinc in manganese-rich spherule identifies the presence of zinc-sorbed birnessite (blue), a layered manganese compound with zinc above and below vacant sites.

A. Manceau, B. Lanson, M. L. Schlegel, J.-C. Hargé, M. Musso, and J.-L. Hazemann (Université J. Fourier and CNRS, France); D. Chateigner (University of Maine-Le Mans, France) and G. M. Lamble (ALS). [*Am. J. Sci.* **300**, 289 (2000)]

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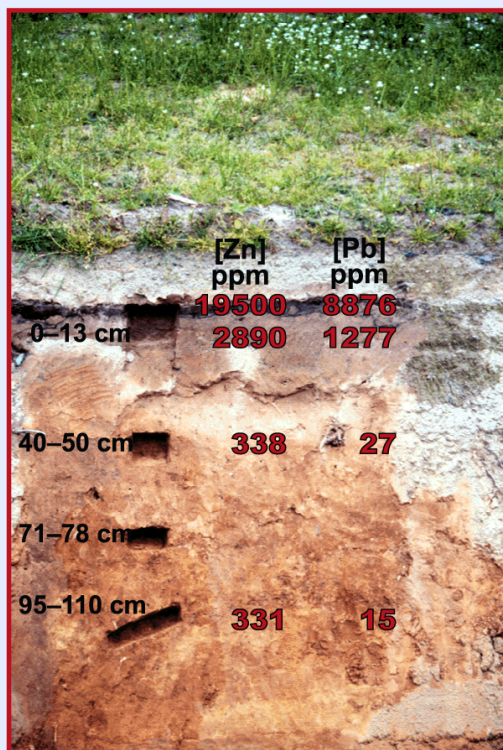
Soils samples at a contaminated site were taken at several depths.

Powder-EXAFS spectra of a soil sample and a combination of model compounds.
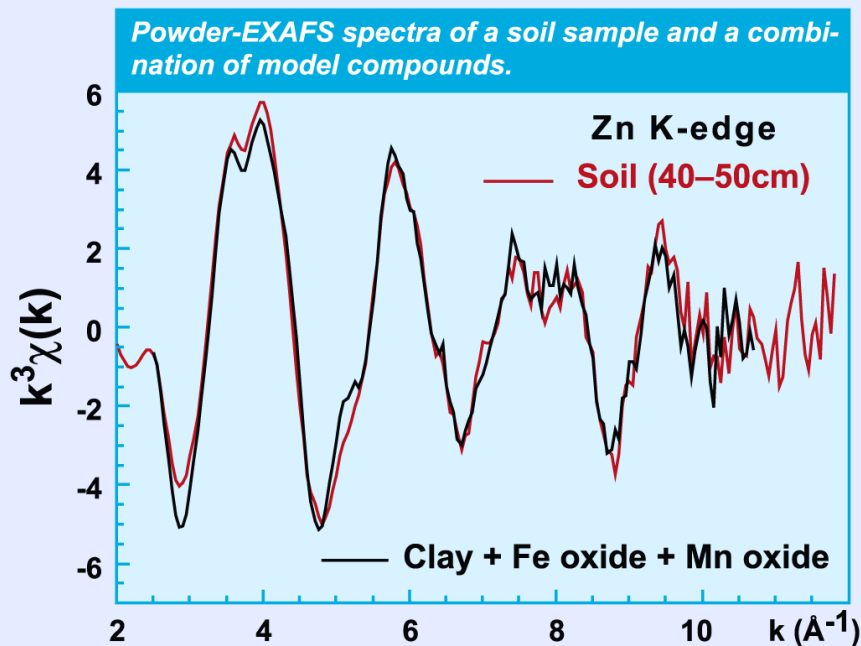
Model compounds derived from polarized-EXAFS data at the ESRF and µ-EXAFS data at the ALS provide a good fit with powder-EXAFS spectra from a soil sample.

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D. Chateigner (University of Maine-Le Mans, France) and G. M. Lamble (ALS). [*Am. J. Sci.* **300**, 289 (2000)]